Name of Organization: Colorado State University

Type of Organization: College or University

Contact Information: Dr. Rajiv Bhadra

Department of Chemical and Bioresource Engineering

Glover Building, Room #100

Fort Collins CO 80523

Phone: (970) 491 - 2227 **Extension:**

Fax: (970) 491 - 7369

E-Mail: rajivb@lamar.colostate.edu

Project Title: Determination of Chloroaromatic Fate in Phytoremediation

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested ($): 132,754 **Project Duration:** 2 Years

Abstract:

The overall goal of this project is to provide a solutions-oriented knowledge base for the phytoremediation of chlorinated aromatic contamination of lacustrine sediments. The project is proposed as a laboratory pilot study to facilitate field applications. The specific objectives are: (i) to quantify rates of sediment-plant transfer of chlorinated aromatic pollutants; (ii) to identify major pathways of fate and metabolism of chlorinated aromatics in plants; and (iii) to determine the effect of environmental parameters on rates of sediment-plant transfer of chlorinated aromatic pollutants. The proposed studies are aimed at both in situ applications for sediment-water environments, and upland dredged sediments. Consequently, both aquatic and terrestrial plants will be employed in this study in two types of plant systems: sediment column systems, and sediment-water column systems. Small-scale plant systems will be directed at analyzing chloroaromatic fate, while larger-scale plant systems will be employed to investigate the effect of environmental parameters relevant to process design for contaminated sediment environments -- sediment quality, redox potential and dissolved oxygen concentration -- on trophic transfer and transfer rates. Overall, a full development of the study approach and outcomes outlined here will yield substantial benefit for rational action and clean-up of chloroaromatic-contaminated sediments.

Geographic Areas Affected by the Project

States:

- [x] Illinois
- [x] Indiana
- [x] Michigan
- [x] Minnesota
- [x] New York
- [x] Pennsylvania
- [x] Wisconsin
- [x] Ohio

Lakes:

- [ ] Superior
- [ ] Huron
- [ ] Michigan
- [ ] Erie
- [ ] Ontario
- [x] All Lakes

Geographic Initiatives:

- [ ] Greater Chicago
- [ ] NE Ohio
- [ ] NW Indiana
- [ ] SE Michigan
- [ ] Lake St. Clair

Primary Affected Area of Concern: All AOCs

Other Affected Areas of Concern:

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area: Not Applicable

Other Affected Biodiversity Investment Areas:

Problem Statement:

Contamination of lacustrine sediments due to hazardous chlorinated aromatic compounds poses a serious environmental threat in the Great Lakes region. Aroclors, PCP, 2,4,6-trichlorophenol, chlorobenzene and hexachlorobenzene are but a few chlorinated aromatics that rank within the top 100 CERCLA priority pollutants. Phytoremediation is well suited to the cost-effective clean-up of large volumes of sediments contaminated with recalcitrant hydrophobic chlorinated aromatic contaminants, either in situ or with dredged upland sediments. In order to deploy phytoremediation in the field as an effective "off the shelf" technology for this clean-up focus, critical needs exist from both risk reduction and process design perspectives. These include the need to evaluate and/or quantify the following in the context of chlorinated aromatics: (i) significant fate pathways in plants, i.e. uptake, volatilization, transformation or binding; (ii) the effect of environmental conditions on rates of plant processes; and (iii) the bioavailability, and ecotoxicology of plant-mediated treatment outcomes. These needs stem from the insufficient knowledge-base of the behavior of chlorinated aromatic compounds in the presence of plants, and of the residues resulting from plant-mediated treatment outcomes. Consequently, measures of phytoremediation outcomes for chloroaroamtic-polluted sediments are limited due to the insufficient knowledge of desirable plant-associated endpoints.

Project Objectives

To addresses several of the above needs for the phytoremediation of sediments contaminated with chlorinated aromatic compounds, the following focused objectives are being proposed for the research described herein:
(a) to quantify rates of sediment-plant transfer of chlorinated aromatic contaminants;
(b) to identify major pathways of fate and metabolism of chlorinated aromatics in plants; and
(c) to determine the effect of environmental parameters on rates of sediment-plant transfer of chlorinated aromatic contaminants.

Proposed Work Outcome:

Contaminant Chemistry:

The objectives outlined above will be pursued with representative chlorinated aromatic contaminant species, and will comprise the following: PCB congeners (Aroclor); chlorobenzenes, dichlorobenzene (DCB) and hexachlorobenzene (HCB); the chlorophenols, 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP). Aryl substituent groups or the lack of them are prime determinants of availability and biochemical reactivity of chlorinated aromatic compounds. The subset selected for this study includes important chloroaromatic pollutants, as well as encompasses diverse aryl chemistries likely to be encountered in contamnated sediments. Vegetation exposed to these xenobiotics will likely respond with a spectrum biochemical reactivities that include, reduction, aryl hydroxylation, ring cleavage, conjugation and immobilization. Therefore, this selected subset is aligned with the proposed effort to identify significant fate pathways and critical

reactivities in exposed vegetation, and to determine environmental parameters of significance in sediment-plant transfer of chloroaromatics.

Plant Systems:

Plant systems employed will fall into two main categories: aquatic macrophytes, and terrestrial plants. Aquatic macrophytes will be focused on analyzing contaminant fate in sediment-water columns, and the terrestrial plants on dredged piles. For the former, rooted aquatic macrophytes will be selected to maximize plant-contaminant contact. Cattail (Typha sp.) will be the candidate species in this category due to favorable growth and hardiness characteristics across a spectrum of natural conditions. Specific oxygenating species, such as Myriophyllum aquaticum may be included to examine the role of dissolved oxygen influx and biochemical diversity. Alfalfa (Medicago sativa) will be employed in terrestrial systems for many of the same factors. Screening of plant species is not in the scope of this project, and as such not relevant to the proposed objectives. The plant systems will be set up at bench-top scales which will address specific project objectives. Large-scale systems (20-30 liter systems) will be employed for macroscopic analysis of sediment-plant transfer in order to quantify transfer rates and role of environmental conditions. These systems are particularly useful in establishing redox-sensitive zones that are known to exist in sediment-water columns. Small-scale flask and bottle systems (0.5-2-liter systems) designed for rigorous mass-balance analysis of all constituent phases - sediment, water column, gas-phase, and plant biomass - will be employed for studies on fate and metabolism.

Environmental Parameters

The effects of sediment quality, redox potential and dissolved oxygen on rates of sediment-plant transfer and post-uptake fate pathways will be examined in this project. Several grades of sediments will be included to examine their effect on sediment-contaminant-plant association and transfer rates. The high octanol-water partition coefficients (Kow) of most chlorinated organic contaminants, particularly PCBs, favor sediment-contaminant interaction. This bulk-phase parameter may not, however, serve as a reliable measure of contaminant bioavailability in the root zone of plants, or of pore-water interactions of sediment-bound hydrophobic in the root zone of plants; this has been shown recently for PAHs (J. Pardue, 1999). Redox potential and dissolved oxygen are also likely to play significant roles as environmental determinants of several aspects of sediment-plant transfer of contaminant, including: biochemical reactivity in plant roots, biochemical reactivity in the sediment rhizosphere due to microbial activity, and chemical speciation of degradation intermediates. Artificially contaminated and 'aged' sediments, as well as historically contaminated sediments, will be employed in this study segment.

Fate and Residue Analysis

To facilitate the analysis of significant pathways of fate and metabolism of chlorinated aromatic contaminants in sediment-plant systems, contaminated sediments will be spiked with the appropriate 14C-labeled compounds. This will facilitate a rapid mass balance analysis on the entire system, which will be independent of the identity of the fate products and contaminant metabolites in the test plants. Mass balance compartments at the system level will include the sediment, water, gas, and plant phases. This analysis will yield such parameters as trophic transfer factors and overall bioconcentration factors. To further investigate contaminant fate and metabolism within exposed (test) plants, root versus shoot analysis will be performed to determine such fate as accumulation and translocation. Residue analysis will be performed in this segment to determine biochemical transformation pathways and to broadly categorize the types of biochemical speciation occurring in test plants. A range of analytical capabilities will be focused on this effort, including: GC-MS, HPLC, radiolabel scintillation analysis, infrared spectroscopy, enzymatic hydrolysis, and selective extractions.

Proposed Outcome

The study proposed herein will facilitate the knowledge-based application of phytoremediation, a rapidly emerging remediation technology, to the treatment of chlorinated aromatic contamination of lacustrine sediments in the Great Lakes environment. This research will yield benefits not only to the engineering manipulation of treatment scenarios for these recalcitrant pollutants, but also to evaluating risk posed by sediment-plant contaminant transfer in existent settings and to evaluating risk mitigation by treatment processes. The anticipated benefits of this proposed research is founded on the deliverables: rates of sediment-pant transfer of chlorinated aromatic contaminants, significant fate in the sediment-plant environment, significant fate and metabolism within exposed plants, and the role of environmental conditions. Overall, a full development of the study approach and outcomes outlined here is likely to yield substantial benefit for rational action and

clean-up of chloroaromatic-contaminated sediments.

Project Milestones:	Dates:
Project Start	10/2000
Uptake Study - Chlorobezenes, Complete	12/2000
Uptake Study - Chlorophenols, Complete	03/2001
Uptake Study - PCB, Complete	06/2001
Fate Analysis - CPs & CBs, Complete	12/2001
Fate Analysis - PCB, Complete	04/2002
Environmental Effects Studies, Complete	08/2002
Project End & Final Report	09/2002

☐ Project Addresses Environmental Justice

If So, Description of How:

☒ Project Addresses Education/Outreach

If So, Description of How:

This project will serve to train several graduate and undergraduate research assistants in methods of inquiry, analysis and problem solving relevant to environmental pollution mitigation. More specifically, it will bring about a scientific and engineering know-how of not only the deleterious and complex consequences of sediment contamination due to chloroaromatic wastes, but also of novel and cost-effective technologies to manage these serious challenges. This endeavor will contribute valuably as well towards the approach of regional practitioners in tackling issues of contaminated river sediments. In addition, members of the project team will disseminate the project findings to peer audiences at scientific conferences and community audiences at stakeholder meetings.

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	49,504	4,896
Fringe:	5,077	198
Travel:	1,530	0
Equipment:	0	0
Supplies:	13,260	0
Contracts:	0	0
Construction:	0	0
Other:	29,642	0
Total Direct Costs:	99,013	5,094
Indirect Costs:	33,741	2,292
Total:	132,754	7,386
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Description of Collaboration/Community Based Support:

A collaboration is planned with Professor Howard S. Ramsdell of the Department of Environmental Health at Colorado State University. Professor Ramsdell is an expert on environmental ecotoxicology, and would serve in a consulting capacity on biolgical indicators of chloroaromatic mitigation in phytoremediation systems. This is not a budgeted commitment, but one with intellectual content that will benefit both the PI's research proposed research as well as Dr. Ramsdell's ongoing research program.